

TITLE
PROTECTIVE LAYERS COMPATIBLE WITH THICK FILM PASTES

FIELD OF THE INVENTION

5 The present invention relates to a process for using a special protective layer for the fabrication of electronic devices that use thick film pastes.

TECHNICAL BACKGROUND

10 The present invention relates to a process for constructing electronic devices wherein a substrate is coated with a conducting layer that is further coated with a thick film paste. The thick film paste may contain materials such as glass frit, various conductors, photo-imageable polymers and, usually a solvent. In the fabrication of these devices photo-definable protective layers may be used to isolate photoimageable thick film deposits from other elements of these electronic devices such as conductive layers. A problem arises in some of these devices in that the solvent used in the thick film pastes, usually an ester or ether type solvent, is frequently aggressive to the polymer protective layer and may lead to short circuits. This can lead to problems on the surface of the substrate 15 such as pealing or dissolution of the protective layer from the substrate when that layer is exposed to the thick film paste.

20 Wang et al in the Proceedings of the SPIE – The International Society for Optical Engineering (1999) vol. 3906, p. 619-24 describe the electrical characterization of polymer thick film resistors.

25 Fukuda et al (US 5601638) describes a thick film paste for use in the formation of circuit components.

 Ezaki (US5362927) reports a thick film hybrid circuit board device formed by lamination.

30 Kazunori et al (JP 2001155626 A) provide a method for producing a display substrate.

 Takehiro and Shigeo (JP10340666 A) describe a field emission element.

 Kazunori and Shinsuke ((JP 2001111217 A) provide a method of forming laminated wiring.

35 The present invention addresses the problem of incompatability of the thick film paste and the protective layers on the substrate by fabricating a protective layer from positive photo-imageable materials

which do not degrade or dissolve upon contact with the high boiling ester-type or ether-type solvents found in the photo-imageable thick film pastes.

SUMMARY OF THE INVENTION

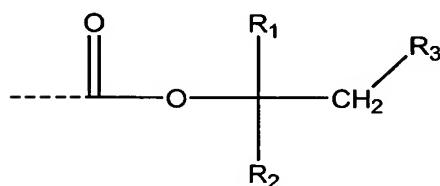
The present invention addresses the problem of compatibility of the
5 thick film paste with a protective layer by fabricating a protective layer from positive photo-imageable materials made of polymers with pendant acid labile groups which do not degrade or dissolve upon contact with the high boiling ester-type or ether-type solvents found in the photo-imageable thick film pastes, e.g. such solvents include butyl carbitol, butyl carbitol
10 acetate, dibutyl carbitol, dibutyl phthalate, texanol and terpineol.

The invention is a process for making an electronic device comprising:

coating an electronic device structure with a positive photo-imageable protective layer comprising a polymer in which at least 50 mole
15 percent of the monomers in the polymer comprise a structure selected from the group consisting of:

(a)

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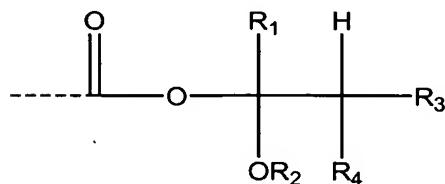


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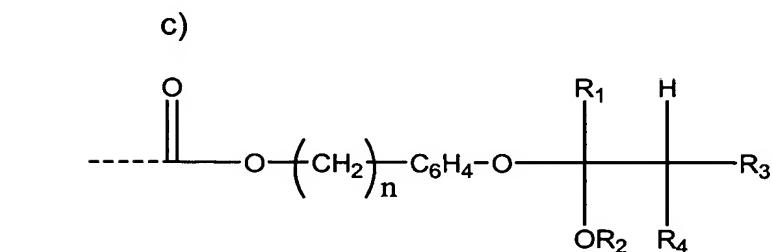
where R₁ is hydrogen or lower alkyl; R₂ is a lower alkyl; and R₃ is hydrogen or a lower alkyl where the definition of lower alkyl includes alkyl groups having 1 to 6 linear or cyclic carbon atoms;

b)

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where R₁ is hydrogen or lower alkyl; R₂ is a lower alkyl; and R₃ and R₄ are independently hydrogen or a lower alkyl where the definition of lower alkyl includes alkyl groups having 1 to 6 carbon atoms and the joining of R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ to form a
5 5-, 6-, or 7-membered ring; and



10

where R₁ is hydrogen or lower alkyl; R₂ is a lower alkyl; and R₃ and R₄ are independently hydrogen or a lower alkyl where the definition of lower
15 alkyl includes alkyl groups having 1 to 6 carbon atoms and the joining of R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ to form a 5-, 6-, or 7-membered ring.

Suitable polymers for the above process are selected from the
20 group consisting of 1-ethoxyethyl methacrylate, 1-ethoxyethyl acrylate, 1-butoxyethyl methacrylate, 1-butoxyethyl acrylate, 1-ethoxy-1-propyl methacrylate, 1-ethoxy-1-propyl acrylate, tetrahydropyranyl methacrylate, tetrahydropyranyl acrylate, tetrahydropyranyl p-vinylbenzoate, 1-ethoxy-1-propyl p-vinylbenzoate, 4-(2-tetrahydropyranyloxy)benzyl methacrylate, 4-(2-tetrahydropyranyloxy)benzyl acrylate, 4-(1-butoxyethoxy)benzyl methacrylate, , 4-(1-butoxyethoxy)benzyl acrylate t-butyl methacrylate; t-butyl acrylate, neopentyl methacrylate, neopentyl acrylate, 1-Bicyclo{2,2,2}octyl methacrylate (or acrylate) and their derivatives, 1-Bicyclo{2,2,1}heptyl methacrylate (or acrylate) and their derivatives, 1-Bicyclo{2,1,1}hexyl methacrylate (or acrylate) and their derivatives, 1-Bicyclo{1,1,1}pentyl methacrylate (or acrylate) and their derivatives and 1-adamantyl methacrylate (or acrylate) and their derivatives.
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In a preferred embodiment, the process further comprises adding to the photo-imageable polymer 0.5-30 mole% of photoacid generator and 10-1000 ppm of photosensitizer.

The invention also includes electronic devices fabricated by the above
5 process.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a photomask grid of a photoresist of the present invention irradiated 120 seconds through a mask followed by heating 10 minutes at 110 C and then washed with carbonate and air dried.

10 Figure 2 shows the grid of Figure 1 following further irradiation without mask followed by heating 10 minutes at 110 C.

Figure 3 shows the grid of Figure 2 after washing with ethyl acetate solvent.

15 Figure 4 shows the grid of Figure 3 after washing with carbonate solution.

DETAILED DESCRIPTION

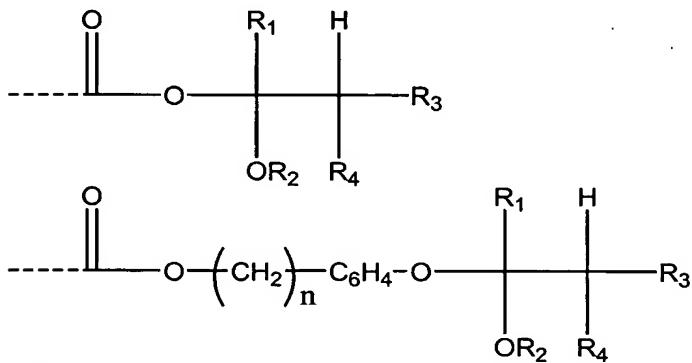
Currently, "novalac-type" of phenolic formaldehyde polymeric materials are typically used as protective layers in the fabrication process of electronic devices utilizing photo-imageable thick film pastes, such as
20 Fodel® silver paste commercialized by DuPont, Wilmington DE. The role of such a protective layer is to maintain spacing between the thick film deposit and other substrate structures to prevent contamination of the bottom substrate with the thick film paste. As mentioned above, in some cases, contamination of the bottom substrate may lead to short circuits.
25 The protective layer is then removed by dissolution along with the unimaged thick film material is removed. However, these protective layers are frequently found to be damaged during the process of applying the paste materials on the top of the protective layer. The cause of the damage is either the dissolution of the protective layer by solvent vapors
30 generated during the paste drying process or plastic deformation of the resist material due to plastization by these vapors. Butyl carbitol, butyl carbitol acetate, dibutyl carbitol, dibutyl phthalate, texanol and terpineol are examples of the solvents currently used in thick film paste formulation.

The present invention uses protective materials that show either lower solubility or improved compatibility toward high boiling ester-type or ether-type solvent vapor so as to reduce the damage of the protective layer. New polymers to be used as a protective layers in electronic device

5 fabrication using photo-imageable thick film pastes must be soluble in an organic solvent so that the polymer can be applied as a thin film on the top of prefabricated device layers. Upon either chemical treatment or photo-irradiation the polymer becomes impervious to ester-type or ether-type organic solvents used in the formulation of the thick film paste. Since the

10 polymer must undergo a photo-imaging step to be used as the protective layer, it must be formulated with a photo-responsive agent. A preferred polymer for this function contains a labile pendant group on a side acid functional group, which can be removed from the polymer pendant group at an appropriate time. One type of pendant acid labile groups useful in

15 the compositions of this invention can be described by the formulae:



20 n=0 to 4;

R₁ is hydrogen or lower alkyl; R₂ is lower alkyl; and R₃ and R₄ independently are hydrogen or lower alkyl where the definition of lower alkyl includes alkyl groups having 1 to 6 carbon atoms and the joining of R₁ and R₂, or R₁ and either R₃ or R₄, or R₂ and either R₃ or R₄ may be

25 joined to form a 5-, 6-, or 7-membered ring.

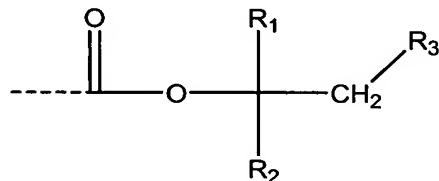
Some examples of acid labile monomeric components that fall within the scope of the invention when used to prepare the polymeric material are:

1-ethoxyethyl methacrylate (or acrylate),

1-butoxyethyl methacrylate (or acrylate),
 1-ethoxy-l-propyl methacrylate (or acrylate),
 tetrahydropyranyl methacrylate (or acrylate),
 tetrahydropyranyl p-vinylbenzoate,
 5 1-ethoxy-l-propyl p-vinylbenzoate, 4-(2-tetrahydropyranyloxy)benzyl
 methacrylate (or acrylate),
 4-(1-butoxyethoxy)benzyl methacrylate (or acrylate).

This is not meant to be a comprehensive list and the invention is not
 10 limited to these materials.

Another type of pendant acid labile groups useful in the
 compositions of this invention can be described by the formulae:



15

R_1 is hydrogen or lower alkyl; R_2 is lower alkyl; and R_3 is hydrogen or lower alkyl where the definition of lower alkyl includes alkyl groups having 1 to 6 linear or cyclic carbon atoms

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Some examples of acid labile monomeric components that fall within the scope of the invention when used to prepare the polymeric material are:

- t-butyl methacrylate (or acrylate),
- Neopentyl methacrylate (or acrylate)
- 25 1-Bicyclo{2,2,2}octyl methacrylate (or acrylate) and their derivatives
- 1-Bicyclo{2,2,1}heptyl methacrylate (or acrylate) and their derivatives
- 1-Bicyclo{2,1,1}hexyl methacrylate (or acrylate) and their derivatives
- 30 derivatives

1-Bicyclo{1,1,1}pentyl methacrylate (or acrylate) and their derivatives

1-adamantyl methacrylate (or acrylate) and their derivatives

5 This is not meant to be a comprehensive list and the invention is not limited to these materials.

The preferred molecular weight of these polymers is 7,000-1,000,000. It is also desirable to use copolymers, either random or block copolymers of monomer units containing those acid labile side groups and
10 some other monomers which do not have acid labile pendant groups but have hydrophilic groups such as ethylene glycol ethers or carboxylic acid groups. Molecular weights higher than typical photoresist known in the field are preferred since the remaining polymer film has to withstand certain mechanical processes, such as screen printing. Mechanical stress
15 is applied to the film with a rubber squeeze during or after the screen printing. In order to improve organic solvent resistance, it would be desirable to have a high amount of acid after the removal of the labile groups. The amount of monomer in the copolymer suitable for imperviousness to the organic vapor depends on the types of organic
20 solvent used with the paste. The preferred mole fraction for the monomer containing labile ester group is 50 %, and the more preferred mole percentage is higher than 60%.

Block copolymers can be prepared by well know methods in art, using
25 methods typically known as living or controlled polymerization, like anionic or group transfer polymerization as well as atom transfer polymerization. The terms and techniques regarding living, controlled, and atom transfer polymerization are discussed in "Controlled/Living Radical Polymerization", edited by K. Matyjaszewski, Oxford University Press.
30 Random copolymers can be obtained by solution polymerization using typical free radical initiator, such as organic peroxide and azo initiators. Discussion of these polymerization methods can be found in "Polymer Chemistry" Fifth Edition by C. E. Carraher Jr, Marcel Dekker Inc. , New

York, New York. (see Chapters 7,8 and 9) or "Polymers" by S. L. Rosen in The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, John Wiley and Sons Inc., New York (see volume 19, pp 899-901).

- 5 The photo initiator is selected from common photo acid generators, such as aromatic sulfonium phosphofluoride or antimony fluoride, or aromatic iodonium salt with similar anions. The photo acid generators, and examples of such compounds, are described in a paper by J. V. Crivello, "The Chemistry of Photoacid Generating Compounds" in Polymeric
- 10 Materials Science and Engineering, Vol. 61, American Chemical Society Meeting, Miami, FL., Seot. 11-15, 1989, pp. 62-66 and references therein. The selected photo acid generator should not undergo decomposition or dissolution during the development stage. Nonionic photoacid generators, such as PI-105 (Midori Kagaku Co , Tokyo, Japan) or high moleuclar
- 15 weight photo acid generators, such as CyraCure UVI 6976 (Dow, Midland, Michigan), CD-1012 (Aldrich Chemical, Milwaukee, WI) are examples of such photo acid generators.

- 20 To fabricate a device using the present invention, a 0.5 to 5 micron thick polymer coating of polymers with pendant labile acid groups and photo-active reagents is applied to a substrate. Such coatings could be achieved by spin coating or table coating using a blade in an appropriate organic solvent. The preferred organic solvents for applying the coating
- 25 are Propylene Glycol 1-Monomethyl Ether 2-Acetate (PGMEA) or cyclohexanone. Next, the solvent is removed by heating the substrate to between 70 to 100 C for typically 1 to 3 minutes on a hot plate. The coating is now ready to be patterned by UV photo-irradiation. UV irradiation followed by heat treatment will cleave acid labile pendant group
- 30 to convert the ester to the acid. The UV photoirradiation source may use 193 nm laser radiation or a mercury lamp. For the higher wavelength than 248 nm may require addition of a small amount (10-1000 ppm) of photosensitizer which increases the absorption of UV light. The examples

of photosensitizer include, but not limited to isopropylthioxanthone (ITX), 2,4-Diethyl-9H-thioxanthen-9-one (DETX), benzophenone. UV irradiation dose is 50 to 1000 mJ/square centimeter. Post exposed baking conditions are typically 120 to 140 C for 1 to 3 minutes. This treatment results the
5 exposed area being soluble in a aqueous base developing solvent. The basic developing solvents may include a carbonate solution or a low concentration sodium or potassium hydroxide solution. Preferably, commercial aqueous base developer, such as AZ 300, 400 or 500, obtained from Clariant Corporation, AZ Electronic Materials Somerville, NJ
10 08876-1258, can be used. After development, a patterned template is formed. The remaining protective film is still soluble in organic solvents, thus its protective function toward the thick film paste is limited. The film can be converted to a film containing a high level of polycarboxylic acid which is insoluble in the common organic solvents employed in thick film
15 pastes by exposure to UV light and subsequent heat treatment. The UV irradiation dose is 50 to 2000 mJ/square centimeter. Post exposed baking conditions are typically 120 to 140 C for 1 to 3 minutes.

The negatively imageable thick film paste of interest is aqueous base
20 developable paste, such as Fodel silver paste commercialized by DuPont, Wilmington DE. It also includes such paste containing carbon nanotubes for field emission display applications. Thick film paste is applied on the top of the converted protective layer by such methods as screen printing, filling the vacancies in the patterned template generated by photo
25 development. Subsequently, the thick film paste is photo irradiated from the back side of the structure. The paste located in the patterned template where the protective film is removed by photoimaging would be imaged preferentially. The paste is negatively developed upon irradiation, so that the paste becomes insoluble to developing solvents. Typically, these thick
30 film pastes are developed by gentle spray of an aqueous base solution. The unimaged paste is washed out within certain time which is called the time-to-clear (TCC). Typically, the spray will last 1.5 to 3.0 times the TTC. The irradiated protective layer is soluble in the aqueous base solution so

that it is removed while the unimaged thick film paste is being removed as it is spray developed.

EXAMPLES

Example 1.

5 1.5 grams of poly(ethoxytriethylene glycol methacrylate-*b*-t-butyl methacrylate), with degree of polymerization (D.P.) of 37/100 and number average molecular weight (M_n) of 28,600, was used. To this was added 0.5 grams CyraCure® UVI-6976 (Dow Chemical), and 0.002 grams Quanticure ITX (Aldrich). All additions were dissolved to a clear solution in 4 ml 2-butanone.

10 Using a 2 mil doctor blade, the solution was cast on MYLAR® (DuPont, Wilmington, DE) film and allowed to air dry for 10 minutes. The film was then dried for 30 minutes in a 100°C convection oven. The dried film was cut into 2.5 X 2.5 cm squares. The film was treated according to the following procedure and examined after each step.

15 A film square was placed in a Plexiglas® sample holder and backed by KAPTON® (DuPont, Wilmington, DE) film. A 50 micron photomask grid was placed over the top of the film and held in place by a large glass disk. The film was exposed to UV light for 120 seconds. The exposed film was then heated to 20 110°C for 10 minutes on a hot plate. The film was washed for 60 seconds using a spray gun with a 0.5% solution of sodium carbonate, followed by a 30 second rinse with distilled water. The film was dried with a stream of N₂. Figure 1 shows the alternating grid of UV irradiated and unirradiated film. In the region designated 1, the irradiated film is dissolved away by the carbonate solution. In 25 the unirradiated, masked region, designated 2, the film is still present. The film was then heated to 110°C for 10 minutes on a hot plate. The film was exposed a second time for 120 seconds with no photomask. The film was then heated to 110°C for 10 minutes on a hot plate. Figure 2 shows the film after irradiation. The area designated 2A has now been irradiated. The surface of the film was 30 washed with ethyl acetate soaked on a Q-Tip and allowed to dry. The ethyl acetate simulates the solvents present in a thick film paste. Figure 3 shows that the area of the film 2A is still intact after exposure to the ethyl acetate. The film was washed for 60 seconds with a 0.5% solution of sodium carbonate, followed

by a 30 second rinse with distilled water. The film was dried with a stream of N₂. Figure 4 shows all of the film has been dissolved.

Example 2

5 0.183 grams of a copolymer of poly(ethoxytriethylene glycol acrylate-*random*-t-butyl methacrylate), (mole ratio of 70:30 of monomers, Mn=10,400, and a polydispersity, PD=2.8), 0.045 grams of DP=5 homopolymer of t-butyl methacryllate, 0.081 grams CyraCure® UVI-6976 (Dow Chemical), and 0.13 milligrams Quanticure ITX (Aldrich) and 0.13
10 mg of 2,3-Diazabicyclo[3.2.2]non-2-ene, 1,4,4-trimethyl-, 2,3-dioxide (TAOBN) (Hampford Research, Inc. P.O. Stratford, Connecticut 06615) were dissolved to a clear solution in 0.424 grams of PGMEA. Using a 2 mil doctor blade, the solution was cast on a glass plate and allowed to air dry for 10 minutes. The film was then dried for 2 min at 70 deg C hot
15 plate. The film was exposed with approximate 600 mJ/cm² broad band UV light using a 20 micron photomask, then heat treated on a hot plate at 120 deg C for 2 min. The imaged part was developed by dipping into a 0.5 % sodium carbonate solution. The film was washed with deionized water for 1 min., then dried on a hot plate at 70 deg C for 1 min. The remaining
20 film was flood exposed with 600 mJ/cm² then heat treated at 120 deg C for 2 mins. The remaining film could be washed out with a 0.5 % sodium carbonate solution.

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Example 3

0.183 grams of a copolymer of poly(ethoxytriethylene glycol acrylate-*random*-t-butyl methacrylate), (mole ratio of 70:30 of the monomers, Mn=10,400), 0.045 grams of DP=5 homopolymer of t-butyl methacryllate, 0.081 grams CyraCure® UVI-6976 (Dow Chemical), and 0.13 milligrams Quanticure ITX
30 (Aldrich) and 0.02 g of BHT were dissolved to a clear solution in 0.424 g of PGMEA. Using a 2 mil doctor blade, the solution was cast on a glass plate and allowed to air dry for 10 minutes. The film was then dried for 2 min at 70 deg C hot plate. The film was exposed with approximate 600 mJ/cm² broad band UV

light using a 20 micron photomask, then heat treated on a hot plate at 120 deg C for 2 min. The imaged part was developed by dipping into a 0.5 % sodium carbonate solution. The film was washed with deionized water for 1 min., then dried on a hot plate at 70 deg C for 1 min. The remaining film was flood

5 exposed with 600 mJ/cm² then heat treated at 120 deg C for 2 mins. The remaining film could be washed out with a 0.5 % sodium carbonate solution.

Example 4

1.097 grams of a copolymer of poly(methylmethacrylate-*random-*
10 methacrylic acid-*random-t-butyl methacrylate*), (mole ratio of 50:50:100 of the monomers, Mn=70,000, PD=3.1), 0.272 grams of DP=5 homopolymer of t-butyl methacryllate 0.485 grams CyraCure® UVI-6976, and 0.08 grams Quanticure ITX (Aldrich) and 0.08 grams TAOBN were dissolved to a clear solution in 2.546 grams of PGMEA. Using a 2 mil doctor blade, the solution was cast on a
15 glass plate and allowed to air dry for 10 minutes. The film was then dried for 2 min at 70 degrees C hot plate. The film was exposed with approximate 1500 mJ/cm² broad band UV light using a 20 micron photomask, then heat treated on a hot plate at 120 degrees C for 2 min. The imaged part was developed by dipping into a 0.5 % sodium carbonate solution.